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ORIGINAL ARTICLE

Biosorption of Cr(III) and Cr(VI) species from aqueous solution by *Cabomba caroliniana*: kinetic and equilibrium study

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Abstract This study reports the potential ability of non-living biomass of *Cabomba caroliniana* for biosorption of Cr(III) and Cr(VI) from aqueous solutions. Effects of contact time, biosorbent dosage, pH of the medium, initial concentration of metal ion and protonation of the biosorbent on heavy metal–biosorbent interactions were studied through batch sorption experiments. Cr(III) was sorbed more rapidly than Cr(VI) and the pH of the medium significantly affected the extent of biosorption of the two metal species differently. Surface titrations showed that the surface of the biosorbent is positively charged at low pH while it is negatively charged at pH higher than 4.0. Protonation of the biosorbent increased its capacity for removal of Cr(III), while decreasing that of Cr(VI). FT-IR spectra of the biosorbent confirmed the involvement of –OH groups on the biosorbent surface in the chromium removal process. Kinetic and equilibrium data showed that the sorption process of each chromium species followed pseudo second-order kinetic model and both Langmuir and Freundlich isothermal models. A possible mechanism for the biosorption of chromium species by non-living *C. caroliniana* is suggested.

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Keywords *Cabomba caroliniana* · Chromium biosorption · Protonation · Surface titration · Kinetics · Isothermal models

Introduction

Discharge and disposal of industrial effluents contaminated with heavy metals have resulted in the pollution of valuable land and water resources. As heavy metals are non-biodegradable and toxic to biological systems, they are of concern to human and animal health. In developing countries, where enforcement of environmental regulations is less stringent, heavy metals enter the food chain through agricultural production. Among many heavy metals used in industries, chromium and its compounds are widely used in leather tanning, chromium plating, metal cleaning and processing, wood preservation, alloy preparation, rust and corrosion inhibition, and the manufacture of dyes and pigments, owing to special characteristics of this heavy metal (Jacques et al. 2007; Mohanty et al. 2006). Consequently chromium, which primarily exists as the soluble, highly toxic Cr(VI) and less soluble, less toxic Cr(III), is one of the most commonly found heavy metals in wastes and/or wastewaters (Karvelas et al. 2003; Mohanty et al. 2006). In the presence of oxidising agents such as MnO_2, oxidation of aqueous Cr(III) to Cr(VI) is more likely to occur, whereas under reducing conditions such as environments rich in organic matter and Fe(II), Cr(VI) is reduced into Cr(III). Further, under acidic conditions, the dissolved Cr(III) concentration can be higher than the World Health Organization (WHO) permissible limit of 0.05 mg L^{-1} for drinking water (Richard and Bourg 1991). Drinking water is one of the common pathways for heavy metals to enter the human body. As many sources of

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drinking water are being contaminated by industrial discharge, chromium level in drinking water is also highly concerned. The health hazards of chromium in humans include cancer in the kidney and lungs, gastrointestinal pain, nausea, vomiting and diarrhoea (MSDS 2012). Thus, pre-treatment of effluents containing either form of chromium, before their discharge into the environment, is necessary to reduce environmental pollution, to safeguard the health of humans.

Several conventional physico-chemical methods, such as membrane filtration (Yoon et al. 2009), chemical precipitation (Matlock et al. 2002; Ramos et al. 2009), ion exchange (Inglezakis and Loizidou 2007), chemical oxidation or reduction (Mitra et al. 2011), electrochemical treatment (Rana et al. 2004), solvent extraction (Miretzky et al. 2006) and activated carbon adsorption (Malik 2003) have been used to remove heavy metals and other contaminants from effluents. However, these methods are not economical, require expensive equipment and generate secondary waste. Further, removal of metals by these methods could be incomplete at low metal concentrations. Therefore, there is a necessity for cost-effective, alternative technologies for the treatment of metal-contaminated aqueous and non-aqueous systems.

Biosorption of heavy metals utilizes the ability of non-living biological materials to accumulate such metals from waste streams by either metabolically mediated or purely physico-chemical pathways of uptake (Fourest and Roux 1992; Mohanty et al. 2006). The uptake of heavy metals by non-living biomass takes place by the passive mode, where the performance of any biosorbent depends on anionic ligands, such as carboxyl, sulphate, phosphate and hydroxyl groups present in the biomass, and on physico-chemical characteristics (Volesky 2003). As these factors control the extent of removal, their effects should be considered in biosorption. A wide range of non-living biomass, such as *Pinus* bark (Alves et al. 1993), *Spirogyra spp.* (Gupta et al. 2001), *Eichhornia crassipes* (Mohanty et al. 2006), yellow passion fruit shell (Jacques et al. 2007), tea factory waste (Malkoc and Nuhoglu 2007), palm flower (Elangovan et al. 2008), orange waste (Marín et al. 2009), vineyard pruning waste (Karaoğlu et al. 2010), lignin (Albadarin et al. 2011) and mill tree bark (Netzahuatl-Muñoz et al. 2012) has been used as biosorbents for the removal of chromium. These studies have shown that the extent of removal of chromium from aqueous solutions by biosorbents depends on pH, contact time, biosorbent dosage, shaking speed and initial concentration of the metal ion. It has also been shown that hydroxyl (Mohanty et al. 2006), carboxylic (Jacques et al. 2007) and amine groups (Gupta and Rastogi 2009; Srividya and Mohanty 2009) are responsible for chromium binding.

Cabomba caroliniana is an aquatic plant that grows extensively as a weed. Although heavy metal removal by many other aquatic plants has been investigated, a comprehensive study on the removal of Cr(III) and Cr(VI) by *C. caroliniana* has not been reported. This article presents, for the first time, a comparative study on equilibrium and kinetic aspects of biosorption of Cr(III) and Cr(VI) from aqueous solutions by non-living biomass of *C. caroliniana*. The surface of the biosorbent was characterised through surface titration and Fourier transform infrared (FT-IR) analysis. Several parameters which affect the extent of the biosorption, such as shaking time, pH of the medium and protonation of the sorbent were optimized through batch sorption experiments. Equilibrium data and kinetics of the sorption process were also studied.

Materials and methods

Sampling of biosorbent

Cabomba caroliniana, or fanwort, available in abundance in tropical countries, is a fully submerged aquatic plant, which belongs to the family Cabombaceae. It is a perennial, aquatic herb growing in ponds, lakes and streams. It is generally rooted in water 1–3 m deep, but grows free-floating if uprooted (Cabomba species 2012).

Fresh *C. caroliniana* were collected randomly from a water stream in Kandy, Sri Lanka, and washed thoroughly with tap water, followed by deionized water. The biomass was air-dried for 2 days and oven-dried at 70 °C for 3 days (higher temperatures were not used to avoid possible decomposition of organic matter). The dried biomass (biosorbent) was ground and sieved to obtain the fraction of diameter between 297 and 350 μm to be used in all experiments, conducted in triplicate whenever necessary.

Chemicals and reagents

Analytical grade chemicals and reagents were used in all experiments. Potassium dichromate and chromium(III) sulphate (both from BDH, Pool, England, UK) were separately dissolved in deionized water to prepare standard test solutions of Cr(VI) and Cr(III), respectively.

Instrumentation

The pH of solutions was measured by a pH meter (Thermo Russell Model RL060P). Chromium was analysed by atomic absorption spectrophotometer (AAS) (Model GBC 933AA) at the wavelength of 357.9 nm using N_2O-acetylene flame. Absorbance of methylene blue was measured with a UV–Visible spectrophotometer (Shimadzu Model UV-160 A) at the wavelength of 665 nm. A microwave digester (Milestone Model START D) was used to digest

the biosorbent. FT-IR spectra of the biosorbent before and after adsorption of chromium species were recorded using Fourier transform infrared spectrophotometer (Model NICOLET 6700). The sample disks used for FT-IR analysis were prepared in anhydrous KBr and the spectral range varied from 4,000 to 400 cm^{-1}. For all sorption equilibrium studies, biosorbent–metal ion suspensions were shaken on an orbital shaker at a rate of 140 rpm to allow interaction between the two phases.

Surface titrations

Nitrogen gas was bubbled through a suspension of 1.0 g of biosorbent in 100 mL of $NaNO_3$ solution of known concentration while stirring at a constant rate for 3 h to remove dissolved CO_2. The vessel containing the suspension was sealed, and stirring was continued for 12 h in a CO_2-free environment to obtain a homogeneous solution. The initial pH of the suspension was measured and a NaOH solution of known concentration was added to reach a known higher pH value of 10.0. The mixture was then titrated by adding small aliquots of HNO_3 of known concentration, and the pH was measured after each addition. The system was allowed to have an adequate equilibration time after each addition before recording the pH measurement. The titration was continued until the pH of the system reached a value of 3.0. The system was continuously and steadily stirred and purged with N_2 throughout the titration. A back titration was carried out using the same NaOH solution while a blank titration was conducted in the absence of the biosorbent. The entire procedure was repeated for two more ionic strengths.

Determination of surface area

The specific surface area of the biosorbent particles was determined by the methylene blue adsorption method (Hang and Brindley 1970). A series of methylene blue solutions of different concentrations ranging from 1.0×10^{-6} to 5.0×10^{-6} mol L^{-1} was prepared. Biosorbent suspensions were then prepared by mixing 5 mg of the biosorbent in 100 mL of each methylene blue solution and stirred gently for 3 h to ensure that adsorption equilibrium was reached. Suspensions were centrifuged and the supernatants were analysed for remaining methylene blue concentration.

Effect of contact time

Different dosages of biosorbent (1.0, 2.0, 4.0 g/L) were thoroughly mixed individually with 100.0 cm^3 of 5.00 mg L^{-1} of metal ion solutions at pH 5.0 and at 25 °C in Erlenmeyer flasks, and the suspensions were shaken as explained earlier under "Instrumentation". The experiment was conducted in triplicate, and the suspensions were removed from the shaker at predetermined time intervals and filtered. The filtrates were analysed for residual chromium concentrations by AAS. The native biomass was digested in nitric acid using a microwave digester, to determine the presence of chromium on it before the sorption process.

Effect of pH

To study the effect of pH on the biosorption processes, 200 mg of the biosorbent was thoroughly mixed individually with 100 mL of metal ion solutions at ambient temperature, each of which was prepared at a different pH between 1.0 and 9.0 using HNO_3 and NaOH solutions. The suspensions were shaken, allowed to settle and the filtrates were analysed for residual chromium by AAS.

Protonation of the biosorbent

For this purpose, 10 g of the biosorbent was introduced into 300 mL of 0.10 M HNO_3 and the suspension was stirred for 6 h. The biosorbent was then separated from the acid medium, washed thoroughly with deionized water until neutral pH and dried at 70 °C. The resulting protonated biosorbent was investigated for its chromium removal ability.

Adsorption isotherm study

Batch isothermal studies were conducted by shaking 0.200 g of dry biomass suspended in 100.0 cm^3 of metal solutions whose initial concentration varied from 1.0 to 18.0 mg L^{-1} at pH 5.00 and at 25 °C. Upon equilibration, suspensions were filtered and the filtrates were analysed for residual chromium concentrations by AAS.

Results and discussion

Surface titrations

The surface charge density (σ) at each pH was calculated using Eq. (1) (Priyantha et al. 2009).

$$\sigma = \{[F/(a \times s)]\}\{(C_a - C_b) - [H^+] + [OH^-]\} \quad (1)$$

where F is the Faraday's constant (96,490 C mol^{-1}), a is the mass of the biosorbent in the suspension (1.0 g), C_a and C_b are the calculated concentrations of the acid and the base, respectively, in the medium at a particular point of titration, $[H^+]$ and $[OH^-]$ are the hydrogen and hydroxyl ion concentrations in the medium according to the

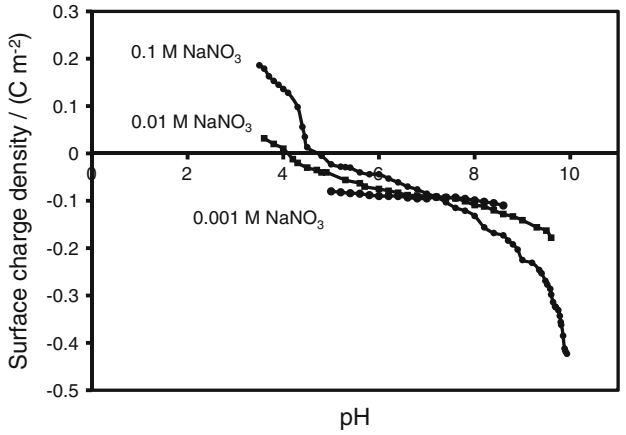

Fig. 1 Variation of surface charge density of *C. caroliniana* with solution pH at different ionic strengths

measured pH value at a particular point of titration. The specific surface area (s) was estimated to be 2.6 $m^2\ g^{-1}$ using Eq. (2),

$$s = M_{mb} \times 6.02 \times 10^{23} \times A_{mb}/m \quad (2)$$

where M_{mb} is the number of moles of methylene blue adsorbed for the completion of a monolayer, A_{mb} is the surface area per methylene blue molecule (130 $Å^2$) and m is the amount of the biosorbent in the suspension (5 mg).

The surface charge of the biosorbent was determined to be highly dependent on the pH of the medium, and the surface charge density versus pH curves plotted for different ionic strengths intersect at a common point of pH = 7.2 (Fig. 1). As the number of protons bound to the surface of the biosorbent is calculated to obtain the ultimate result of surface charge density, it is assumed that no other ion other than protons in the medium binds to the biosorbent during surface titrations (Butt et al. 2003). The importance of using $NaNO_3$ in surface titrations is that its constituent ions do not bind specifically to the biosorbent surface.

According to Fig. 1, the biosorbent surface is positively charged at low pH, which becomes negative at pH > 5 for ionic strengths between 0.001 and 0.1 M, which includes typical concentrations of ions in wastewater. Thus, positively charged ions, such as Cr(III), would be preferentially attracted to the surface of the biosorbent when the pH is maintained at pH > 5. Increase in surface charge with increase in ionic strength is due to the increase in the capacitance of the electric double layer resulting in increased charge for a given surface potential (Butt et al. 2003).

Effect of contact time

The percentage removal of Cr(III) and Cr(VI) by *C. caroliniana* are shown as a function of shaking time in Fig. 2. These values were determined using Eq. (3), where C_i and C_f are the initial and the final concentrations, respectively, of each metal in the system, both of which were determined by AAS measurements.

$$\text{Percentage removal} = [(C_i - C_f)/C_i] \times 100 \quad (3)$$

The results show that the extent of metal ion removal by the biosorbent initially increases with the increase in contact time and reaches the equilibrium where it showed the maximum removal. The removal of Cr(III) and Cr(VI) achieved the equilibrium point after 10 and 125 min, respectively, and these two time periods were thus considered as the optimum shaking times for each chromium species. Initial rapid sorption probably involves physical adsorption or ion exchange at the cell surface and the subsequent slower sorption may involve other mechanisms such as complexation, micro-precipitation or saturation of binding sites (Gupta and Rastogi 2009). As predicted by surface charge studies, it is clear from Fig. 2 that *C. caroliniana* removes Cr(III) more preferentially than Cr(VI). The adsorption capacity of *C. caroliniana* in comparison with that of other biosorbents reported is shown in Table 1. According to Table 1, *C. caroliniana* is able to remove significant amounts of Cr(III) more rapidly than by many other biosorbents. Further, the protonated form of the biosorbent is more efficient for Cr(III) removal in terms of equilibration time and removal capacity. Among many biosorbents, higher removal of Cr(VI) by lignin (87.5 %) and by *Catla catla* scales (57 %) were achieved with a high initial metal concentration and longer equilibration time (Srividya and Mohanty 2009; Albadarin et al. 2011). Although the capacity of Cr(VI) removal by *C. caroliniana* is less, when all the conditions (i.e., sorbent dose, initial metal concentration and pH) are considered, *C. caroliniana* shows a competitive performance with other biosorbents.

The percentage removal of both metal ions increased with the increase of the sorbent dosage (Fig. 2). This increase in biosorption with the increase in the biosorbent dose is due to a higher surface area available for chromium binding (Albadarin et al. 2011). When the biosorbent dose was increased from 1.0 to 2.0 g L^{-1}, the maximum removal of Cr(III) and Cr(VI) increased by 11 and 16 %, respectively. On the other hand, when the dose was increased from 2.0 to 4.0 g L^{-1}, Cr(III) removal increased by 24 % while the increase of removal of Cr(VI) remained at 16 %. This further supports the preferential interaction of Cr(III) with the biosorbent surface.

Effect of pH

The characteristics of the biosorbent and the nature and the extent of speciation of a metal ion in solution depend on the pH of the solution (Volesky 2003). Therefore, the

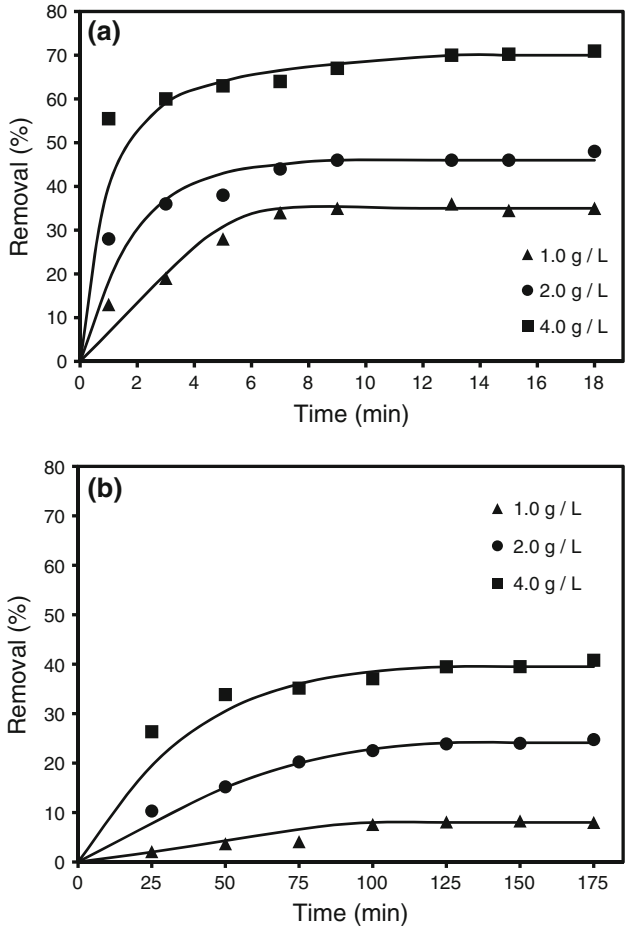

Fig. 2 Percentage removal of **a** Cr(III) and **b** Cr(VI) by different doses of dry *C. caroliniana* biosorbent at different shaking times (initial metal ion concentration = 5.0 mg L^{-1}, pH = 5.0, temperature = 25 °C, shaking speed = 140 rpm)

acidity of the medium is an important parameter among many other factors in biosorption studies (Aksu and Isoglu 2005; Amarasinghe and Williams 2007; Dhakal et al. 2005; Gupta et al. 2001; Jacques et al. 2007; Malkoc and Nuhoglu 2007; Mohanty et al. 2006; Sciban et al. 2006). Even if the pH was properly controlled, the ionic strength and the type of ionic and non-ionic constituents would influence the extent of interaction between the ions in solution and the solid biosorbent. Consequently, the effect of solution pH on the extent of removal of ionic species from solution is a complex issue. Therefore, it is important to keep the ionic strength and the type of buffer components unchanged during pH dependent studies. The percentage removal of Cr(III) and Cr(VI) as a function of the pH of the metal ion solution is shown in Fig. 3. The variations of removal with pH for the two oxidation states of the same metal are different from each other. The optimum pH for the maximum biosorption of Cr(VI) is 2.0, whereas that of Cr(III) is 5.0. Two factors important in explaining this result are the charge of the metal ion in solution and the surface charge of the biosorbent at a particular pH. In aqueous media, Cr(III) exists as a positively charged ion, while Cr(VI) exists as negatively charged $Cr_2O_7^{2-}$ ions. At low pH, owing to the positive surface charge of the biosorbent, negatively charged Cr(VI) species bind more favourably through electrostatic forces, whereas the positively charged Cr(III) species are repelled by the biosorbent (Malkoc and Nuhoglu 2007; Mohanty et al. 2006; Tarley and Arruda 2004). Further, competition of H^+ at low pH values also contributes to low removal of Cr(III) at higher H^+ concentrations. As the pH is increased, the surface charge density of the biosorbent becomes negative (Fig. 1) so that the repulsion between Cr(III) and the biosorbent surface is reduced and consequently the adsorption of Cr(III) increases, whereas that of Cr(VI) decreases.

Further, extremely high and low pH would damage the structure of the biosorbent and consequently, the sorption capacity toward both chromium species decreases significantly as observed. Such observations are common for many natural adsorbents (Volesky 2003).

FT-IR investigation of biosorption

To determine the types of functional groups responsible for the removal of chromium species, FT-IR analysis was performed on the biosorbent before and after the sorption process. The FT-IR spectrum of the biosorbent (Fig. 4) displays a number of vibrational bands, indicating the complex nature of the biosorbent. Table 2 shows the changes in the major peak positions in the FT-IR spectrum of the biosorbent, before and after contact with chromium solutions. Absence of peaks in the frequency region of 1,700–1,725 cm^{-1}, which is the region for C=O stretching of carboxylic acids, confirms the absence of carboxylic acid groups in the biosorbent. When the FT-IR spectra of the chromium-loaded biosorbent are compared with that of the original biosorbent, bands responsible for the stretching of hydroxyl groups shifted their central positions significantly by 25.0 and 66.6 cm^{-1} for Cr(III) and Cr(VI) species, respectively, indicating the involvement of hydroxyl groups in the biosorption process (Mohanty et al. 2006).

Kinetics of the sorption process

Kinetic parameters of an adsorption process are essential for the evaluation of adsorption parameters, which in turn control the entire process of sorption, which are thus important for designing sorption systems. The sorption kinetics of a system are controlled by different steps, including transfer of solute to the sorbent particle surface, transfer from the sorbent surface to the intra-particle active sites and retention on these active sites via sorption, complexation or intra-particle precipitation phenomena

Table 1 Comparison of Cr(III) and Cr(VI) adsorption capacity of *C. Caroliniana* with that of different biosorbents

Biosorbent	Sorbent dose (g L^{-1})	Metal ion concentration (mg L^{-1}) (oxidation state of Cr)	pH	Contact time (min)	Removal capacity (mg g^{-1}) and its percentage	Reference
Palm flower	10	25 [Cr(III)]	4.5	120	2.0 (82.7 %)	Elangovan et al. 2008
Orange waste	2.0	100 [Cr(III)]	4.0	4,320	25.0 (50 %)	Marín et al. 2009
Vineyard pruning waste	5.0	15 [Cr(III)]	4.2	15	2.07 (69 %)	Karaoğlu et al. 2010
Cupressus lusitanica	1.0	100 [Cr(III)]	5.0	10,080	56.0 (56 %)	Netzahuatl-Muñoz et al. 2012
C. caroliniana (non-protonated)	2.0	5 [Cr(III)]	5.0	10	1.15 (46 %)	Present study
C. caroliniana (protonated)	2.0	5 [Cr(III)]	5.0	10	2.45 (98 %)	Present study
Spirogyra Spp.	3.0	5 [Cr(VI)]	5.8	120	0.3 (20 %)	Gupta et al. 2001
Eichhornia crassipes	1.0	10 [Cr(VI)]	5.8	40	2.1 (21 %)	Mohanty et al. 2006
Tea factory waste	10.0	100 [Cr(VI)]	5.0	30	3.7 (37 %)	Malkoc and Nuhoglu 2007
Catla catla scales	2.0	15 [Cr(VI)]	5.4	180	4.3 (57 %)	Srividya and Mohanty 2009
Oedogonium hatei (protonated)	0.8	50 [Cr(VI)]	2.2	110	15.0 (24 %)	Gupta and Rastogi 2009
Oedogonium hatei (non-protonated)	0.8	50 [Cr(VI)]	2.2	110	13.0 (20 %)	Gupta and Rastogi 2009
Lignin	2.0	50 [Cr(VI)]	2.0	1,440	21.8 (87.5 %)	Albadarin et al. 2011
C. caroliniana (non-protonated)	2.0	5 [Cr(VI)]	5.0	120	0.6 (24 %)	Present study
C. caroliniana (protonated)	2.0	5 [Cr(VI)]	5.0	120	0.07 (3 %)	Present study

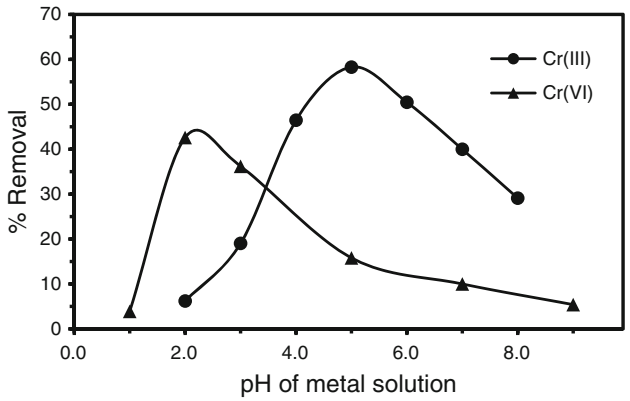

Fig. 3 Effect of pH on biosorption of Cr(III) and Cr(VI) on dry *C. caroliniana* biosorbent [biosorbent dosage = 2.0 g L^{-1}, initial metal ion concentration = 5.0 mg L^{-1}, temperature = 25 °C, shaking time = 10 min for Cr(III) and 125 min for Cr(VI), shaking speed = 140 rpm]

(Shroff and Vaidya 2011). To determine the controlling mechanism of the biosorption process, different kinetic models were employed to test the experimental data.

Pseudo first- and second-order kinetic models

Pseudo first-order kinetic model and the pseudo second-order model (Jacques et al. 2007; Mohanty et al. 2006; Shroff and Vaidya 2011) were tested, to investigate the order of the sorption of the metal ions on *Cabomba caroliniana*.

The pseudo first-order kinetic equation is expressed as follows:

$$\ln(q_e - q_t) = -k_1 t + \ln q_e \quad (4)$$

The pseudo second-order kinetic equation is expressed as follows:

$$1/q_t = 1/\left(k_2 q_e^2 t\right) + 1/q_e \quad (5)$$

where q_e and q_t denote the amounts of metal ions sorbed per unit mass of the sorbent (mg g^{-1} dry biomass) at equilibrium and at time t, respectively. k_1 and k_2 are the pseudo first-order rate constant (min^{-1}) and the pseudo second-order rate constant (g mg^{-1} min^{-1}), respectively. The amount of metal ions sorbed on to biosorbent was calculated by using the following equation (Jacques et al. 2007):

$$q = (C_0 - C_f)V/m \quad (6)$$

where q is the amount of metal ion sorbed by the biosorbent (mg g^{-1} dry biomass), C_0 is the initial metal ion concentration (mg L^{-1}), C_f is the metal ion concentration (mg L^{-1}) after biosorption process, V is the volume (L) of metal ion solution kept in contact with the biosorbent and m is the mass (g) of biosorbent.

The experimental data were plotted under each model. The values of k_1, k_2 and q_e of each sorption process were determined from the slopes and intercepts of the plots and presented in Table 3 along with their relevant regression coefficients (R^2). Relatively higher R^2 values and more or

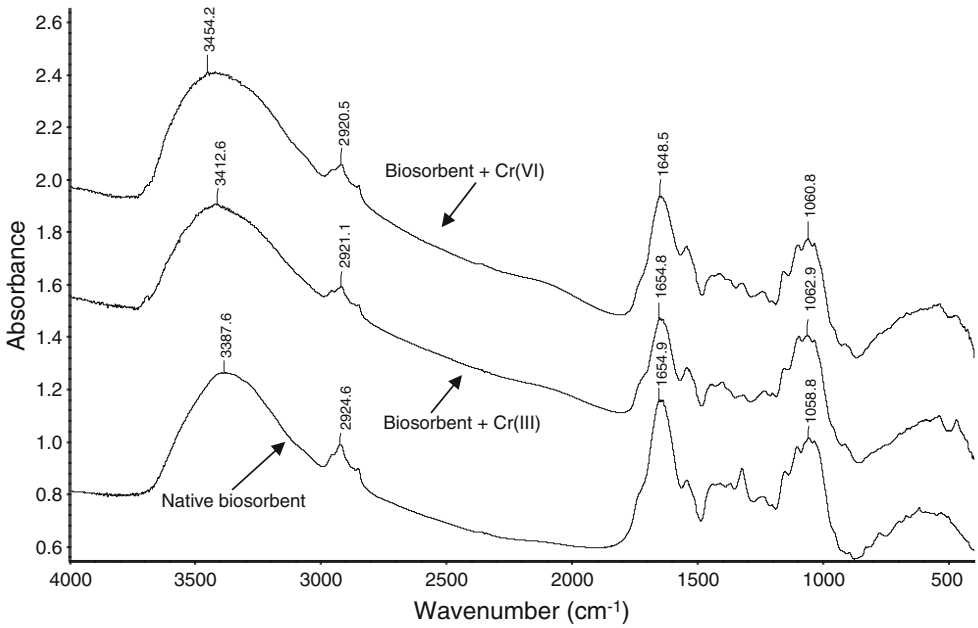

Fig. 4 FT-IR spectra of the biosorbent before and after contact with chromium ion solutions

Table 2 FT-IR spectral bands in the *C. Caroliniana* before and after contact with Cr(III) and Cr(VI) solutions

FT-IR band wavenumber (cm^{-1})			Functional group assignment	Reference
Before Cr removal	After Cr(III) removal	After Cr(VI) removal		
3,388	3,413	3,454	Bonded O–H	Jacques et al. 2007
2,925	2,921	2,920	Methylene asymmetric C–H stretching	Pavia et al. 2009
2,853	2,851	2,851	Methylene symmetric C–H stretching	Pavia et al. 2009
1,655	1,655	1,648	Aliphatic C=C stretching	Pavia et al. 2009
1,059	1,063	1,061	C–O stretching of primary alcohols	Jacques et al. 2007
1,036	1,036	1,036	C–O stretching of ethers	Netzahuatl-Muñoz et al. 2012

less closer experimental q_e and calculated q_e values showed a better agreement of biosorption processes of both Cr(III) and Cr(VI) with the pseudo second-order kinetic model, which indicates that the rates of these biosorption processes depend on both the concentration of the metal ion species and the concentration of biosorbent (Jacques et al. 2007; Shroff and Vaidya 2011). This model also indicates that the rate-limiting step is a biosorption mechanism involving chemisorption, where removal of metal ion from the solution is purely due to physico-chemical interactions between the biosorbent and the metal solution (Lodeiro et al. 2006). Similar results have been reported in many other previous publications (Abbas et al. 2008; Du et al. 2011; Jacques et al. 2007; Mohanty et al. 2006; Prahas et al. 2008; Rao et al. 2010; Shroff and Vaidya 2011; Vinod et al. 2010). The higher values of k_2 and q_e obtained for the sorption of Cr(III), explain its rapidness and effectiveness over the sorption of Cr(VI).

Intra-particle diffusion model

The basic assumption of the intra-particle diffusion model is that the film diffusion is negligible and intra-particle diffusion is the only rate-controlling step (Mohan et al. 2007). The mostly applied mathematical expression for the intra-particle diffusion model is given by the Eq. (7) (Mohan et al. 2007; Shroff and Vaidya 2011; Srividya and Mohanty 2009)

$$q_t = k_i t^{0.5} \tag{7}$$

where q_t is the amount of metal ion adsorbed per unit mass of sorbent (mg g^{-1}) at time t (mg g^{-1}) and k_i is the intra-particle rate constant (mg g^{-1} $min^{-0.5}$). According to Eq. (7), the plot of q_t versus $t^{0.5}$ should yield a straight line passing through the origin if the sorption process follows the intra-particle diffusion model. However, the relationships obtained for adsorption of Cr(III) and Cr(VI) on to *C. caroliniana* were not linear over the entire time range and not passing through the origin (Fig. 5), indicating that the intra-

Table 3 Comparison of pseudo first- and second-order kinetic parameters of biosorption of Cr(III) and Cr(VI) by *Cabomba caroliniana* (initial metal ion concentration = 5.0 mg L^{-1}, pH = 5.0, temperature = 25 °C, shaking speed = 140 rpm)

Metal ion	Dose (g L^{-1})	q_e (experimental) (mg g^{-1})	Pseudo first-order			Pseudo second-order		
			k_1 (min^{-1})	q_e (calculated) (mg g^{-1})	R^2	k_2 (g mg^{-1} min^{-1})	q_e (calculated) (mg g^{-1})	R^2
Cr(III)	1.0	2.49	0.374	0.47	0.907	2.061	2.51	0.970
	2.0	1.15	0.289	0.61	0.830	1.528	1.11	0.933
	4.0	0.84	0.322	0.21	0.958	4.182	0.85	0.984
Cr(VI)	1.0	0.22	0.029	0.53	0.724	0.016	0.41	0.949
	2.0	0.59	0.033	0.99	0.942	0.019	0.87	0.984
	4.0	1.12	0.020	0.55	0.950	0.052	1.22	0.984

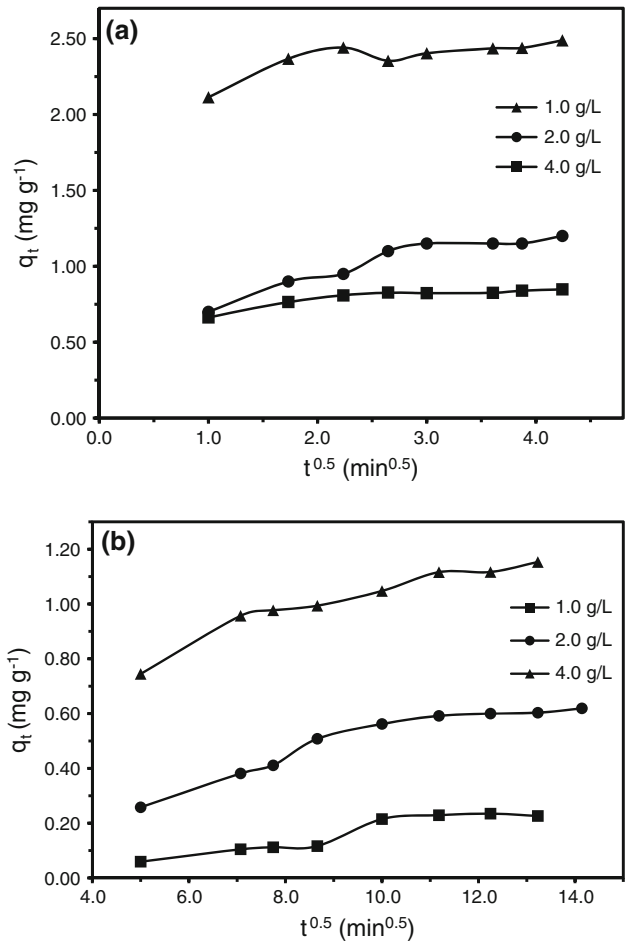

Fig. 5 Intra-particle diffusion for **a** Cr(III) and **b** Cr(VI) sorption onto *C. caroliniana* biomass (initial metal ion concentration = 5.0 mg L^{-1}, pH = 5.0, temperature = 25 °C, shaking speed = 140 rpm)

particle diffusion is not the only rate-controlling step (Mohan et al. 2007; Mohanty et al. 2006; Shroff and Vaidya 2011).

Adsorption isotherms

Analysis of the sorption equilibrium data is important for designing of a biosorption system (Malkoc and Nuhoglu 2007; Srividya and Mohanty 2009). Hence the data, obtained from isothermal study, were tested with Langmuir and Freundlich models.

The linear form of the Langmuir isotherm model (Langmuir 1916) is given by

$$1/q_e = 1/bq_0C_e + 1/q_0 \quad (8)$$

where q_e is the amount of metal ions sorbed per unit mass of the sorbent (mg g^{-1} dry biomass) at equilibrium, b is the adsorption coefficient, q_0 is the amount of metal ions sorbed per unit mass of the sorbent (mg g^{-1} dry biomass) corresponding to complete coverage of available sites (i.e. monolayer saturation capacity), C_e is the residual metal ion concentration (mg L^{-1}) at equilibrium. The values of b and q_0 were evaluated from the slope and intercept of the linear plot of $1/q_e$ versus $1/C_e$, respectively.

The Freundlich isotherm model (Mohanty et al. 2006) is expressed as

$$\ln q_e = \ln k + 1/n \ln C_e \quad (9)$$

where k and n are the constants related to adsorption capacity and adsorption intensity, respectively. These constants were determined from the intercept and slope of the linear plot of ln q_e versus ln C_e, respectively.

Adsorption isotherms for Cr(III) and Cr(VI) are shown in Fig. 6. The experimental data were fitted to both Langmuir and Freundlich isotherms. The isotherm constants and the R^2 values are given in Table 4. As the value of $1/n$ is less than 1 for Cr(III) adsorption, it indicates favourable adsorption (Huang et al. 2010) whereas adsorption of Cr(VI) is unfavourable. Further, Cr(III) shows higher adsorption capacity and affinity compared to Cr(VI).

Effect of protonation of the biosorbent

Chemical treatment such as protonation of the sorbent material enhances the sorption performance of the same systems (Volesky 2003). The protonation of the *C. caroliniana* surface significantly increases the removal of

Cr(III) to 98 %, more than twice the removal by non-protonated biosorption (Fig. 7a). However, the removal of Cr(VI) by the protonated biomass decreased to 3 % (Fig. 7b). These observations suggest the possibility of an ion-exchange process when Cr(III) is interacting with the protonated biomass. Decrease in pH of biosorbent–metal suspensions during the removal process of Cr(III) was also observed and this further supports the involvement of an ion-exchange mechanism during Cr(III) removal. Hence, the protons on the biosorbent surface were more preferably and more conveniently replaced by positively charged Cr(III) ions. However, the adsorption of Cr(VI) in the form of negatively charged $Cr_2O_7^{2-}$ ions is not favoured by protonation of the biosorbent. Further, as the pH decreased during the sorption process, already adsorbed Cr(VI) ions would be replaced by H^+ ions, and consequently reducing the percentage removal at longer contact time periods of the biosorption process (Fig. 7b).

Proposed mechanism for biosorption of Cr(III) and Cr(VI) by dry *C. caroliniana*

Biosorbents are highly complex structures, which consist of many types of binding sites. Moreover, one binding site can participate in different binding mechanisms and the mechanisms may vary with external conditions such as pH. Hence, several mechanisms often act in combination during the biosorption process (Volesky 2003).

The FT-IR spectra of the biosorbent (Fig. 4) confirms that the –OH groups on the biosorbent surface are responsible for chromium binding. As the only shift in IR bands within the range from 4,000 to 1,000 cm^{-1} corresponds to the hydroxyl group, it is proposed that metal ions are bonded to the –OH moiety rather than replacing it. At low pH, hydroxyl groups undergo protonation forming –

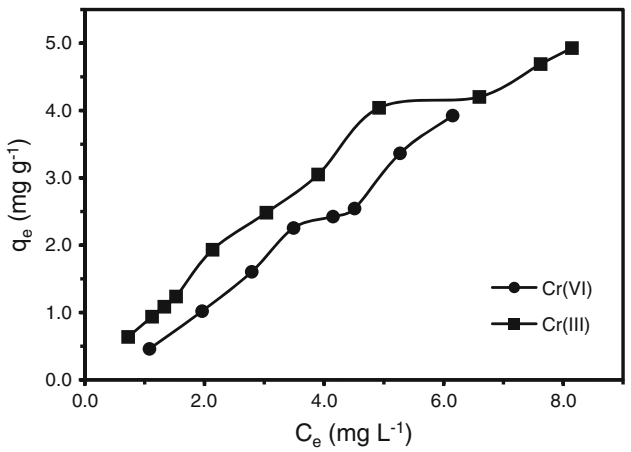

Fig. 6 Adsorption isotherms for Cr(III) and Cr(VI) sorption onto *C. caroliniana* biomass (biosorbent dosage = 2.0 g L^{-1}, pH = 5.0, temperature = 25 °C, shaking speed = 140 rpm)

Table 4 Langmuir and Freundlich isotherm constants for the biosorption of Cr(III) and Cr(VI) by *Cabomba caroliniana* (biosorbent dosage = 2.0 g L^{-1}, pH = 5.0, temperature = 25 °C, shaking speed = 140 rpm)

Metal ion	Langmuir constants			Freundlich constants		
	q_0 (mg g^{-1})	b (L mg^{-1})	R^2	k	$1/n$	R^2
Cr(III)	19.61	0.046	0.996	0.888	0.860	0.986
Cr(VI)	4.74	0.084	0.990	0.440	1.218	0.992

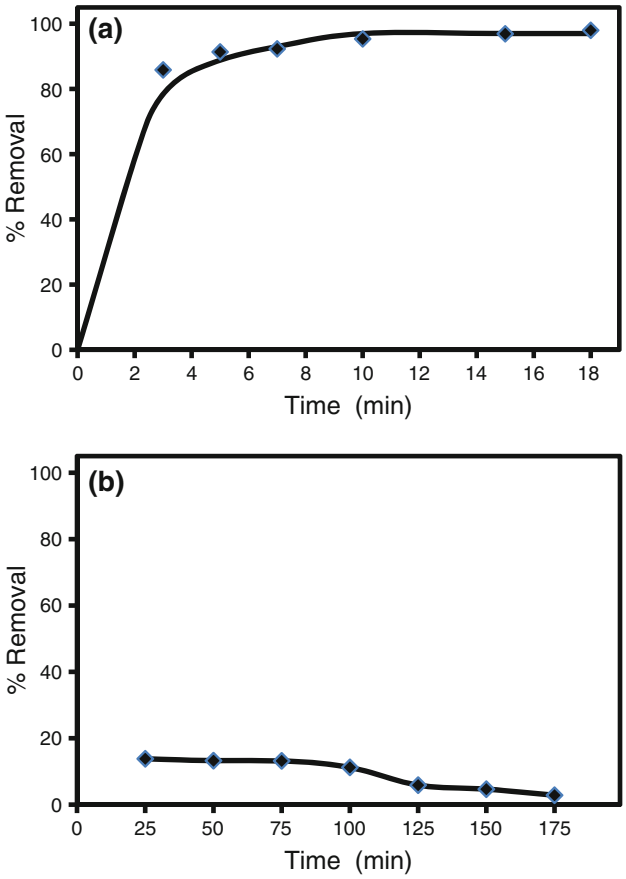

Fig. 7 Percentage removal of **a** Cr(III) and **b** Cr(VI) by dry protonated *C. caroliniana* biosorbent at different shaking times (biosorbent dosage = 2.0 g L^{-1}, initial metal ion concentration = 5.0 mg L^{-1}, pH = 5.0, temperature = 25 °C, shaking speed = 140 rpm, settling time = 15 min)

OH_2^+ terminals (Priyantha et al. 2009). This can be attributed to the positive charge of the sorbent surface at low pH values (Fig. 1). Consequently, Cr(VI) in the form of negatively charged $Cr_2O_7^{2-}$ ions bind more preferentially on to these $–OH_2^+$ terminals on the biosorbent surface through electrostatic attractions. In contrast, when pH increases, surface –OH groups would predominantly exist as $–O^-$ terminals as there would be no protonation, resulting in a negative surface, where positively charged

Cr(III) ions bind more preferentially through electrostatic attractions. On the other hand, Cr(III) may also form coordination bonds with $-O^-$ terminals, as oxygen is a good electron donor atom. Further, ion-exchange between H^+ and Cr(III) species also contributes to the removal process.

When the biosorbent was protonated in 0.10 M HNO_3 solution, ion exchange mechanism predominates over the electrostatic attraction for Cr(III) biosorption and does not favour the biosorption of Cr(VI).

Conclusions

Non-living biomass of *C. caroliniana* was able to remove Cr(III) more rapidly and effectively than Cr(VI) from aqueous solutions. The maximum percentage removals for each chromium species was obtained at the equilibrium point and it increased with the increase of the sorbent dosage. The optimum pH for biosorption of Cr(III) was 5.0, while that of Cr(VI) was 2.0. Protonated biosorbent removed 98 % of aqueous Cr(III). Surface of the biosorbent was positively charged at low pH and negatively charged at pH above 4.0. FT-IR spectra showed that –OH groups on the biosorbent surface were involved in chromium binding process. Kinetics of the sorption processes of both chromium species followed the pseudo second-order kinetic model while their equilibrium data followed both Langmuir and Freundlich adsorption isotherms. Chromium was removed from solution by the biosorbent through an electrostatic attraction mechanism, whereas protonated biosorbent followed an ion exchange mechanism.

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